

Freshwater Quality Monitoring Protocol
San Francisco Area Network

Standard Operating Procedure (SOP) # 5

FIELD METHODS FOR MEASUREMENT OF CORE PARAMETERS

Version 1.01

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Revision History Log

Prev. Version #	Revision Date	Author	Changes Made	Reason for Change	New Version #
1.0	08/05/05	Mary Cooprider	Minor edits	Preparation for formal peer review	1.01

Only changes in this specific SOP will be logged here. “Version numbers increase incrementally by hundredths (e.g. version 1.01, version 1.02, ...etc) for minor changes. Major revisions should be designated with the next whole number (e.g., version 2.0, 3.0, 4.0 ...). Record the previous version number, date of revision, author of the revision, identify paragraphs and pages where changes are made, and the reason for making the changes along with the new version number” (Peitz et al, 2002).

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Appendices

A Field Data Sheet for Core Parameters

B Winkler Titration Method for Dissolved Oxygen

Acknowledgements

Several SOPs and guidance documents were utilized to develop this SOP. Much of the content of this SOP originated in one or more of the following documents:

- ◆ Penoyer, P. 2003. Vital Signs Long-Term Monitoring Projects: Part C, Draft Guidance on WRD Required Parameter Measurements, General Monitoring Methods and some design considerations in Preparation of a Detailed Study Plan (Work in Progress); National Park Service – Water Resources Division
<http://science.nature.nps.gov/im/monitor/protocols/wqPartC.doc> .
- ◆ Puckett, M. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program ("SWAMP"). California Department of Fish and Game, Monterey, CA. Prepared for the State Water Resources Control Board, Sacramento, CA. 145 pages plus Appendices.
- ◆ Wilde, F.D. and Radtke, D.B., eds., chapter sections variously dated, Field Measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, available online at <http://pubs.water.usgs.gov/twri9A>. [National field manual for the collection of water-quality data \(USGS Techniques of Water-Resources Investigations Book 9, Chapter A1-A9\)](#)

- ◆ Shelton, L. 1994. Field Guide for Collecting and Processing Stream-Water Samples for the National Water Quality Assessment Program. Open-File Report 94-455. U.S. Geological Survey, Sacramento, CA.

Standard operating procedures from other parks were also followed including SOP#5 – “Procedures for Collection of Required Field Parameters” from the Greater Yellowstone Network (O’Ney, 2005) and water quality SOPS from the Crissy Field Restoration Area Monitoring Plan (Presidio of San Francisco) (Ward, 2004).

1.0 SCOPE AND APPLICATION

1.1 Core/Required Parameters

The Freshwater Workgroup Subcommittee of the National Park Service – Water Resources Division provided recommendations for required water quality monitoring parameters (National Park Service, 2002). These include:

- 1) Temperature
- 2) Specific conductance
- 3) pH
- 4) Dissolved oxygen

These parameters are considered the “core” parameters for the SFAN Freshwater Quality Monitoring Protocol. These parameters are interrelated and describe the basic water chemistry. They are the first indicators of water quality and typically the simplest to measure. If one or more of these parameters is out of the normal range for a particular stream or does not fall within water quality criteria limits, then concern is raised. The degree of concern is related to the extent that the parameter exceeds criteria or typical ranges and the duration of the exceedence. A one-time exceedence could indicate an episodic pollutant event or an error in measurement. The objective of this SOP is to reduce the possibility of the latter being an option.

Thorough knowledge of these core parameters is also needed in order to better understand or explain levels of other parameters such as nutrients and bacteria. An overview of past monitoring for these core parameters is provided in the *SFAN Preliminary Water Quality Status Report* (Coopridier, 2004). This includes background information on factors affecting the core parameters as well as their typical ranges in SFAN streams. Water quality criteria for these parameters are discussed in the protocol narrative. These criteria will be referenced during data analysis procedures (SOP #10). The core parameters are discussed in greater detail in “Vital Signs Long-Term Monitoring Projects: Part C, Draft Guidance on WRD Required Parameter Measurements, General Monitoring Methods and some design considerations in Preparation of a Detailed Study Plan” (Work in Progress) August 6, 2003 Draft Update (Penoyer, 2003).

The Water Resources Division (WRD) has also noted the importance of flow/discharge measurements, biomonitoring, and alkalinity measurements. The first parameter, flow/discharge, is a critical component of the SFAN Freshwater Quality Monitoring Protocol. The second important parameter, biomonitoring, was included in the list of SFAN Vital Signs but not chosen as a priority indicator. However, recent aquatic bioassessment data exists for many of the SFAN streams. Results of on-going data analyses should provide insight for future possible aquatic bioassessment through the long-term monitoring program. Existing aquatic macroinvertebrate data will provide a baseline for future monitoring efforts. WRD also listed alkalinity as an important indicator. However, it is not an issue in the Bay Area streams since they are well-buffered. Lendvay and Benning (2004) provides a good example of this buffering in Redwood Creek (GOGA).

2.0 MEASUREMENT PROCEDURES

Details of measurement procedures will focus on the use of a waterproof electronic pH meter and a multiparameter probe to measure temperature, specific conductance, and dissolved oxygen. Calibration procedures for these instruments are discussed in SOP#3. **COMPLETE THESE CALIBRATION TASKS BEFORE PROCEEDING.** Flow measurements will be discussed in SOP #9. The following steps provide an overview of field collection techniques for the core parameters:

Details to be covered include:

- ◆ Equilibration of instruments with ambient water
- ◆ Location of sensor/probe within sample site
- ◆ Measurement techniques for flowing water (riffles or glides/runs) vs. standing water (pools)
- ◆ Location of sensor/probe in water column (obtaining a vertical profile)
- ◆ Tips for measuring each parameter
- ◆ Monthly/weekly and continuous monitoring

2.1 Monthly/Weekly Monitoring

Steps in Collection of Field Measurements:

1. Test and calibrate field equipment (SOP #3); clean with deionized water before each measurement
2. Obtain a flow measurement at the cross-section where samples are to be collected (SOP #9)
3. Locate the centroid of flow if sampling in a riffle or run/glide
4. Collect water samples for nutrients, bacteria, and sediment (SOPs #6-8)
5. Allow sensors to equilibrate with ambient water while samples are collected (2 minutes)
6. Complete general information on field data sheet
7. Collect a vertical profile of field measurements
8. Monitor field measurement readings (take mean of readings over 1 minutes, ending with dissolved oxygen)
9. Report the mean value
10. Clean the sensor with deionized water after taking the measurement

2.1.1 Sampling in Riffles/Runs (Centroid of Flow Method)

Standard Operating Procedure #9 for flow/discharge measurements should be followed first. Collect field measurements at the centroid of flow. The centroid is the midpoint of that portion of the stream width that contains 50% of the total flow. This is calculated in the field by adding a “cumulative discharge” column to the flow field sheet. The San Francisco Bay Regional Water Quality Control Board’s SWAMP project uses the centroid of flow method (Puckett, 2002). If the stream is well-mixed with relatively uniform discharge, then the centroid of flow method can be used (Wilde et al., 1999).

If taking measurements in the centroid of flow has the potential to compromise safety, then either wade only to a safe distance or take measurements from the bank. Do not attempt to wade a

stream for which values of depth multiplied by velocity are greater than or equal to 10 ft²/s. For example, a stream only 2 ft deep but with velocities of 5 ft/s or more can be dangerous to wade.

2.1.2 Sampling in Pools

Many of the monitoring questions require sampling in both flowing and still habitats within the stream. For still habitats (pools) the location and number of measurements points depends upon the specific monitoring questions listed in Appendix D of the Protocol Narrative. The USGS National Field Manual indicates that for still waters “measurements made at discrete depths through the vertical water column must not be averaged or reported as a median value.” Pools in SFAN streams and tributaries indicated in the protocol narrative can be up to 3 feet deep during the dry season (May-October) and much deeper during the wet season (November-April). General guidelines for taking field measurements in pools:

The USGS recommends that if a pool is shallow (< 1 ft), take measurements at a middle depth. If the pool is from 1-4 ft deep collect measurements just below the surface, just above the stream bottom (taking care not to bury the probe in sediments) and at a location between the two (Wilde and Radke, variously dated). This can be done for the core parameters but not for laboratory analytes since it would be cost prohibitive.

2.1.3 Equilibration & Stabilization of Sensors

- If water samples are to be collected, then leave the multiparameter probe in the water to equilibrate while samples are collected. Before recording a field measurement, the sensors must equilibrate to the water temperature at the sampling site. Allow a minimum of two minutes for the YSI 85 (multi-parameter probe) to equilibrate to the ambient water temperature. Equilibrate in the D.O. mode (Puckett, 2002). Equilibration has been achieved when the variability among instrument readings has stabilized according to the criteria in Table 1 .
- The natural variability of surface water typically falls within the ranges listed in the table. Therefore, if the instrument is calibrated properly (see SOP #3) then these stabilization criteria should be met.
- Sensors have equilibrated adequately when instrument readings have stabilized, that is, when the variability among measurements does not exceed an established criterion. For surface waters, allow at least 60 seconds (or follow manufacturer’s guidelines) for sensors to equilibrate, then take instrument readings until the stabilization criteria in Table 1 are met. Record the median of the final three or more readings as the value to be reported for that measurement point.
- For sites at which variability exceeds the criteria of Table 1: Allow the instrument a longer equilibration time and record more measurements. To determine the value to be reported for that measurement point, use either the median of the final five or more measurements recorded, or apply knowledge of the site and professional judgment to select the most representative of the final readings. Be sure to note how the measurement was selected in the field notes (Wilde et al., 1999).

- Allow at least 1 minute for sensors to equilibrate with the water. Obtain readings until the stabilization criteria are met. Record the median of the final three or more readings (Wilde et al., 1999).
- If the variability in measurements exceeds the criteria listed in the table, allow a longer equilibration time for the instruments. To select a final reading for the site, use the median of the final five or more measurements recorded or use knowledge of the site and professional judgement to select the most representative final readings (Wilde et al., 1999).
- In order to be efficient, water samples can be collected while the sensors are equilibrating. Leave the multi-parameter probe in the water to equilibrate while samples are collected. Field measurements are generally taken in the same location as water samples are collected (Wilde et al., 1999). Ch. 6

Table 1. Stabilization criteria (from USGS National Field Manual) and WRD recommended instrument stabilization criteria for recording field measurements. Note the units to be used and recommended calibration frequencies.

Standard Direct Field Measurement	Stabilization Criteria For Measurements (variability/repeatability should be within the value shown)
¹ Temperature: Thermistor Thermometer Liquid-in-glass Thermometer	$\pm 0.2^{\circ}\text{C}$ $\pm 0.5^{\circ}\text{C}$
² Conductivity (Specific Cond.) When $\leq 100 \mu\text{S/cm}$ When $> 100 \mu\text{S/cm}$	± 5 percent ± 3 percent
³ pH: Meter displays to 0.01	± 0.1 unit
³ Dissolved oxygen: Amperometric method	$\pm 0.3 \text{ mg/L}$

** Resolution/Sensitivity is a data quality indicator related to detection limits but typically handled differently for field probes than for laboratory parameters. For more information, see Part B (<http://science.nature.nps.gov/im/monitor/protocols/wqPartB.doc>) (Irwin, 2004).

***In the case of field probes, accuracy is typically a “best case” maximum deviation from known correct values (typically based on comparisons with known NIST certified reference materials or standards). True accuracy is a combination of high precision and low bias (see Part B for more details).

¹ Recommended sensor calibration is quarterly

² Recommended sensor calibration is daily

³ Recommended sensor calibration is at beginning and end of sampling at each station (twice a day minimum)

2.1.4 Field Observations

Note the field conditions and general observations on the data sheet in Appendix A. Note the general field conditions including time of day, rain/no rain, rising/falling limb of hydrograph, watercolor, runoff conditions, etc. Also note the land use or any situations out of the ordinary. This data may be useful particularly if unusual parameter readings are observed.

Site information to record includes:

- ◆ Site ID, date, time, field personnel

Field observations to record include:

- ◆ Weather: Time since last rain, current heavy rain, dry, cold, etc.
- ◆ Water color and other characteristics: Unusual amount of suspended solids, debris, foam
- ◆ Biological activity: Note excessive macrophyte (plants), phytoplankton (microscopic floating aquatic plants) or periphyton (microscopic plants and animals firmly attached to aquatic substrate) growth and the presence of birds, fish, and spawning fish
- ◆ Water odors-sewage, hydrogen sulfide
- ◆ In-stream activities-bridge construction, mowing near the stream, livestock watering upstream, etc.
- ◆ Beneficial uses – swimming, wading, irrigation pumps, etc.

2.1.5 Field Measurements

1. Stand downstream of sensors to reduce/eliminate affects of streambed disturbance and/or potential cross-contamination from other sites. Cross-contamination can also be avoided by rinsing field boots as well as the sensors.
2. Go to the centroid of flow as determined above. Obtain measurements directly from the water body by immersing the multiprobe instrument. Allow to equilibrate for at least two minutes before measurements are recorded.
3. Measure at multiple depths within the vertical containing the centroid of flow or within the pool as outlined in Table 2.
4. Monitor field measurement readings (take mean of readings over 1 minute, ending with dissolved oxygen). The value recorded will be the mean of values observed within 1 minute after the sensor has equilibrated.
5. Measure at multiple depths in the vertical. The value recorded at the vertical represents the mean of values observed within approximately 60 seconds after sensor(s) have equilibrated with stream water. Record DO last.
6. The final field-measurement value is the mean of the *in situ* value for the vertical. The mean of pH is calculated as below (see tips for pH measurement)

Depth-integrating and width-integrating sampling methods can be used to collect and composite samples that can then be sub-sampled for some field measurements. The same field measurements can also be performed on discrete samples collected with thief, bailer, or grab samplers. These samples can yield good data for conductivity, pH, turbidity, and alkalinity as

longs correct procedures are followed and the water is not anoxic. Do not measure temperature or DO on subsamples.

Table 2. Recommended Depths for Conducting Field Data Measurements (*from Puckett, 2002*)

Water Depth Less than 5 feet (<1.5m)	If the water depth is less than 5 feet (1.5m), multi-probe measurements are taken at approximately 0.2m (8 in).
Water Depth Greater than 5 feet (>1.5m)	If the water depth at the sampling point exceeds 5 feet (1.5m) in depth, a vertical profile of dissolved oxygen, temperature, pH and specific conductance are made using the multiparameter probe equipment. *NOTE: for most SFAN streams, if the depth is > 5 ft, then the discharge is too great to safely and accurately obtain a vertical profile.
Vertical Depth Profiles and Depth-Integrated Sample Collection	If vertical profile measurements are being conducted, multi-probe measurements are made starting at a depth of 0.2 m (8 in), and are then conducted at 1.0 m (3.28 ft) depth intervals.

2.1.6 Parameter Specific Details and Tips for Measurement

Temperature:

- As a back-up procedure, temperature can be measured with a hand-held, centigrade thermometer.
- In wadeable streams, stand so that a shadow is cast upon the site for temperature measurement.
- Hold the thermometer by its top and immerse it in the water. Position the thermometer so that the scale can be read.
- Ensure that the temperature sensor is completely submerged in the water. Temperature readings made with digital instruments are accurate to within + 0.1° C.
- Air temperature
- Read air temperature with a dry, calibrated thermometer.
- Place the thermometer about 5 ft above the ground in a shaded area protected from strong winds but open to air circulation. Avoid areas of possible radiant heat effects, such as metal walls, rock exposures, or sides of vehicles.
- Allow 3 to 5 minutes for the thermometer to equilibrate, then record the temperature and time of day.
- Measure the air temperature as close as possible to the time when the water temperature is measured.
- Report routine air temperature measurements to the nearest 0.5°C.

pH:

- “Is the value real or is the instrument out of calibration?” Avoid having to guess at an answer by having pH standards in the field to help verify values that fall outside the expected range. For example, the expected pH is around 7.0 and the reading is 9.5. A known standard can be put in the instrument storage cup to determine if the instrument is reading correctly or out of calibration.
- If the pH meter value does not stabilize in several minutes, out gassing of carbon dioxide or hydrogen sulfide, or the settling of charged clay particles may be occurring (Rawson, 1982).
- If out gassing is suspected as the cause of meter drift, collect a fresh sample, immerse the pH probe and read pH at one minute.
- If suspended clay particles are the suspected cause of meter drift, allow the sample to settle for 10 minutes, then read the pH in the upper layer of sample without agitating the sample.
- In low-ionic strength water ($<50\mu\text{S}/\text{cm}$) the pH measurements may not stabilize and a mean or median value must be taken from a range covering several tenths of pH units (Penoyer, 2003).
- To average pH measurements, the pH values must first be converted to the antilog, and average value computed, then converted back to the log value.

To compute a mean pH for the stream:

- Convert each pH value to hydrogen-ion activity, using the equation, Activity = $10^{-(\text{pH})}$.
- Calculate the mean of the activity values by adding the values and dividing the sum by the total number of values.
- Convert the calculated mean activity back to pH units, using the equation, $\text{pH} = (-)(\log_{10})(\text{mean H}^+ \text{ activity})$.

Specific Conductance/Conductivity

- As with pH measurements, having specific conductance standards in the field can help verify values that fall outside the expected range. For example, the expected specific conductance is around 200 and the reading is 1500. A known standard can be put in the instrument storage cup to determine if the instrument is reading correctly or out of calibration.
- Be sure to note the units as conductivity may range from $\mu\text{S}/\text{cm}$ to mS/cm .
- A common physical problem in using a specific conductance probe (or meter) is entrapment of air in the conductivity probe chambers. The presence of air in the probe is indicated by unstable specific conductance values fluctuating up to ± 100 micro-siemens/cm ($\mu\text{S}/\text{cm}$). This can be minimized by slowly, carefully placing the probe into the water; and when the probe is completely submerged, quickly move it through the water to release any air bubbles.
- For specific conductance, the degrees C is flashing; for conductivity it is not flashing. Specific conductance is the conductance measured at 25°C . Since conductivity varies with temperature, it should always be reported as specific conductance.
- Always rinse the conductivity cell with clean water after each use (YSI Inc., 1998)

- Record the “raw” measurement (all digits). When reporting to STORET, round to the nearest two or three significant figures (if the value exceeds 100). If the value exceeds 1000, record to four significant figures.

Dissolved Oxygen:

- Check the sample location sheet for site elevation, calibrate the YSI 85 meter (oxygen probe) for elevation. Keeping the probe in its calibration (storage) chamber, press “mode” until one of the oxygen parameters appears on the screen. Then, press the down and up arrows simultaneously. The screen should have a single large number, then “alt x 100” in the right-hand corner. For an elevation of 400 ft enter 4. See the YSI 85 manual for detailed instructions (YSI, Inc. 1998).
- The DO measurement typically takes the longest to stabilize (Penoyer, 2003). This may take 5-15 minutes in some cases depending upon the water body and the instrument. Record this parameter *after* temperature, conductivity, and pH.
- Since dissolved oxygen takes the longest to stabilize, if the electronic DO meter is not functioning properly, DO can be measured by Winkler titration (Eckblad, 1978). The Winkler titration procedure is described in Appendix B.
- The sensor must be moved back and forth if placed in still water since the sensor consumes oxygen. YSI (1998) recommends that the sensor be moved through the sample at a rate of 1 ft/s to provide sufficient stirring. If the stream velocity at the sampling point exceeds 1 ft/s, the probe membrane can be pointed upstream into the flow and manual stirring can be avoided (Rawson, 1982).
- The probe should never be allowed to penetrate the sediments, especially when DO is low. If the probe does accidentally hit anoxic sediments it should be allowed to re-equilibrate at least a minute before readings are resumed.

Oxygen meters use a polarographic electrode to measure the dissolved oxygen concentration in water. The instrument senses the partial pressure of oxygen at the surface of the membrane, rather than the actual concentration of oxygen (weight/volume). The relationship between partial pressure and concentration is dependent upon atmospheric pressure and temperature when a reading is made in the air (i.e., during the air calibration procedure), whereas, the equilibrium solubility of oxygen in water is influenced by temperature, salinity, and pressure (of the gaseous phase) (Puckett, 2002). Corrections for these factors must be made either by the instrument, by the user during calibration or after readings are taken. The Winkler titration directly measures oxygen equivalents and reports dissolved oxygen concentration (weight/volume) in a form that requires no corrections

2.2 Continuous Monitoring

This section described methods for using an in-situ datalogger, in this case, the Hydrolab minisonde. The minisonde can record data for temperature, conductivity, dissolved oxygen, and pH as well as two additional parameters (with additional sensors). The entire users manual can be found on-line at: http://www.hachenvironmental.com/pdf/Series_4a_Manual.pdf

These methods outlined below are largely adapted from the Crissy Field Restoration Area Monitoring Program Quality Assurance Project Plan (Ward, 2005). The minisonde will most

likely be placed near the streambank in order to be properly secured. The standard procedure is to deploy the data logger 1ft below the surface (need citation). However, the location of the logger will be dependent on the monitoring questions and the depth of the stream. Since the logger must remain fully submerged throughout the year, the location of the logger is often limited to the deepest part of a pool in smaller streams or to a part of a perennial stream with a sufficient water depth to cover the probes. It is recommended that the logger be used continuously for one to two years. However, regular maintenance and calibration requirements dictate how long the logger stays in place.

The Hydrolab® mini-sonde should be left in place for 2 weeks. Leaving it in place for longer than 3 weeks is not recommended since biofouling is likely to occur (Hydrolab Corporation, 1998). After two weeks field personnel should:

1. Use the YSI 85 to obtain measurements adjacent to the Minisonde before removal
2. Remove datalogger from field
3. Conduct post-calibration and cleaning (see SOP#3) (do this after downloading?)
4. Download data
5. Check and/or change batteries and O-rings
6. Conduct pre-calibration
7. Return data logger to field (1 day after it is removed)
8. Record all notes in the data notebook for the instrument and/or site

The YSI 85 should be used to collect concurrent measurements for comparison with the continuous logger at the time of deployment, midway through deployment (approximately 1 week), and at the time of removal. These measurements should be taken at the same depth as the Minisonde and adjacent to it. Measurements should be recorded at a minimum of every hour and a maximum of every 15 minutes.

The data logger should be re-deployed the next day if possible. Datalogger cleaning, calibration, and downloading should be conducted according to the manufacturer's recommendations (Hydrolab Corporation, 1998). Details of these steps are included in SOP #3.

Notes on Continuously Recorded Temperature (from the USGS National Field Manual)

The USGS defines three temperatures of concern when monitoring continuous stream temperature: true stream temperature (TST), temperature near sensor (TNS), and temperature recorded (TRC) (Stevens et al., 1975). Ideally, all three of these temperatures would be the same, however this is not always the case. The true stream temperature is defined as an instantaneous measurement obtained in a shaded location in the main flow of the stream outside of the influence of tributaries or groundwater influx with a full immersion thermometer calibrated against an ASTM standard thermometer. It can also be calculated as the weighted average of a cross-section temperature profile. For reasons of safety and convenience, sensors for stream temperature recorders are often placed closer to shore than would represent true stream temperature (Essig, 1998). The actual temperature of the water surrounding the sensor reflects its position in the channel cross-section, and is known as the temperature near sensor (TNS). Whether it is the same as the TST may vary depending on flow and time of day (Essig,

1998). The temperature recorded (TRC) is the measurement read and recorded. If the thermometer or sensor has been calibrated, then TRC can be adjusted to TNS.

3.0 DATA MANAGEMENT

The SFAN Freshwater Quality Protocol Narrative as well as the overall Data Management Plan should be consulted for a thorough review of data management procedures. A summary of data management tasks is below.

- Record and verify observed or measured data values. This includes completing paper forms and entering data into NPSTORET and/or other electronic databases.
- Schedule and perform regular data transfer and backup.
- Conduct regular data verification and correction
- Ensure that field forms, field notebooks and other hardcopy records are secure, organized and readily available for viewing, reproduction or transfer upon request and/or at the end of each field season.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

The QAPP describes methods used to ensure that the data collected is as representative of the natural environment as possible. Quality assurance procedures are required in all data collection efforts for the long-term monitoring plan. The following should be conducted to ensure the quality of data collected (adapted from O’Ney, 2005):

- Field measurements should be made only with calibrated instruments
- The instruments should be tested and/or calibrated before leaving for the field
- At a minimum, DO and pH shall be calibrated again in the field at the monitoring station immediately before taking measurements
- Practice your measurement technique if the instrument or measurement is new to you.
- Each field instrument must have a permanent log book for recording calibrations and repairs. Review the log book before leaving for the field (see also SOP#3).
- All manually recorded field measurement data should be collected on field forms
- Automatically recorded data should be obtained electronically and the equipment used should be documented on field forms
- Complete records are maintained for each uniquely identified sampling station and all supporting metadata should be recorded appropriately (field forms or electronically)
- Have backup instruments readily available and in good working condition.
- Quality-assurance protocols are mandatory for every data collection effort, and include practicing good field procedures and implementing quality-control checks.
- Make field measurements in a manner that minimizes artifacts that can bias the result.
- Check field-measurement precision and accuracy (variability and bias).
- Check measurement sensitivity

The SFAN Quality Assurance Project Plan (SOP #4) contains all of the details related to QA/QC requirements for field measurements. A summary of this is provided in Table 3 below. Many of the QA/QC procedures are covered in SOP#3- Equipment Preparations: Calibration, Handling, and Storage. However, there are several QA/QC measures for the field. One of these involves calculating measurement sensitivity and is described below.

Table 3. Data Quality Objectives for Field Measurements

Parameter	Instrument or Method	Alternative Measurement Sensitivity (AMS)	Method Detection Limit	Report as: (for STORET)
pH	Oakton pH testr 3+	***	0.01 pH	0.1 units
Dissolved oxygen	YSI 85	***	0.01mg/L	0.1 mg/L
Salinity	YSI 85	***	0.1 ppt	
Temperature	YSI 85	***	0.01	0.2 ⁰ C with a thermistor and 0.5 ⁰ C with a liquid in glass thermometer
Specific Conductance	YSI 85	2.5 uS/cm	0.1 uS/cm	Raw number and rounded number

“Measurement Sensitivity” is a term typically used for laboratory parameters that may often yield results near zero. This is not an issue with field measurements that are always above a “limit of quantitation” (the minimum level of quantitation or ML. The ML is a lower limit below which there is no way to accurately determine (i.e., be 100% sure) how much of a compound such as nitrate is present. However, with field measurements the lower limits are not a concern. For example, specific conductance in a natural stream cannot be zero; there are always ions present and this results in some level of electrical conductivity.

Measurement Sensitivity is used for laboratory parameters while the term “Alternative Measurement Sensitivity” (AMS) is used for field parameters. The AMS is more specifically defined as “the measurement precision uncertainty based on a sample size of seven environmental samples (not blank) and 99% confidence” (Irwin, 2004).

The AMS is calculated as follows:

- Follow the above procedures for equipment equilibration and stabilization
- Follow steps 1-6 for Field Measurements
- Take seven distinct measurements for each parameter at regular intervals
- Take the standard deviation of the seven samples (this can be calculated in Excel) and multiply by 3.707, the t value for a 99% confidence interval and a sample size of 7 (6 degrees of freedom). This number is taken from a standard table of t distribution critical values.

→ Calculate the AMS for each parameter at the beginning of the field season, during the winter (high flow) and at the end of the field season. Once a consistent range is developed, this can be conducted annually.

5.0 REFERENCES

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Appendix A

Field Data Sheet for Core Parameters

SFAN Water Quality Monitoring Program Field Data Sheet

Station ID _____

Site Location _____

Date _____

Time _____ PST

Field Crew _____

Parameter	*Measurement	Units	**Value Type	Instrument	Detection Limit
Temperature					
Conductivity					
Specific Conductance					
Salinity					
Dissolved Oxygen		%			
Dissolved Oxygen		mg/L			
pH					
Flow					

* Take seven measurements at the beginning of each quarter (Oct., Jan., April, July) to obtain standard deviation for calculating PQL

** Actual, Calculated, Estimated

Field Conditions

Notes

Storm event? _____ If so, which storm of the season (1st, 4th, 7th)? _____

Appendix B

Winkler Titration Method for Dissolved Oxygen Measurement

Winkler Titration Method

From Eckblad, J.W. 1978. Laboratory Manual of Aquatic Biology. Wm. C. Brown Company Publishers, Dubuque, Iowa. 231 pp.

If the electronic DO probe is inoperable, DO should be measured by Winkler titration (Texas Natural Resource Conservation Commission, 1997). A Winkler titration kit includes:

- Two 300-mL biochemical oxygen demand (BOD) bottles with stoppers (may substitute a 300-mL Erlenmeyer flask for titration).
- One sewage sampler.
- Manganous sulfate powder pillows.
- Alkaline-iodide-azide reagent powder pillows.
- Sulfamic acid powder pillows.
- 10-mL pipettes; 200- or 250-mL graduated cylinder.
- 0.025*N* phenylarsineoxide (PAO) (replace annually or as needed in field kit).
- Stable starch reagent indicator solution. (Starch solution is stable for 1 month under field conditions. It should be renewed from stock, which is stable for up to 1 year in refrigerator.)
- Scissors or knife for opening powder pillows.

The following steps summarize Winkler titration procedures:

1. Collect a sample for titration by placing a 300-mL BOD bottle in a sewage sampler and lowering the top of the sewage sampler to a depth of 1 ft.
2. The sewage sampler will fill in 30 to 45 seconds.
3. The sampler is filled with water when it ceases bubbling.
4. The sewage sampler should not be withdrawn until it has filled completely.
5. The sampler should be carried upright until the BOD bottle is removed.
6. Carefully remove the BOD bottle from the sewage sampler.
7. The bottle should be filled to the top of the lip.
8. Gently pour the upper 3 to 4 mL of water out of the flared mouth of the bottle.
9. Add the contents of one manganous sulfate powder pillow to the full bottle.
10. Add the contents of one alkaline-iodide-azide reagent powder pillow to the full bottle.
11. Incline the bottle slightly and recap with a glass stopper in a quick, twisting thrust.
12. Do not allow air bubbles to be trapped in the bottle. Sometimes this can be accomplished by just touching the top of the liquid with the stopper tip and then dropping it into position.
13. Invert the bottle at least 25 times to mix completely and then set the bottle aside out of direct sunlight.
14. A brown flocculent indicates the presence of DO. Allow the flocculent to settle halfway down the bottle (approximately 5 minutes).
15. Invert the bottle another 25 times and let the flocculent settle once again. The flocculent will settle very slowly in sea water, which requires a minimum of 2 minutes reaction time. Results will not be affected if the flocculent refuses to settle or if some of the reagent powder does not dissolve.

16. When the flocculent has settled after the second inversion so that the upper one-third of the bottle is clear, or after waiting 2 minutes, add the contents of one sulfamic acid powder pillow.
17. Recap and gently invert the bottle another 25 times until all the flocculent has disappeared. The solution should be clear and straw-colored in appearance. The intensity of the yellow color is related directly to the original concentration of DO in the sample. A clear, pale solution indicates a very low DO concentration. A dark, clear, yellow solution indicates a high DO concentration.

Samples prepared with the addition of sulfamic acid can be stored for 4 hours before completion of the Winkler titration. Samples can be stored for a maximum of 6 hours in the dark if the bottle is stored at the temperature of collection or water-sealed by putting water around the lip and kept at 10 to 20 °C (American Public Health Association, 1995).

As soon as the precipitate has completely dissolved as a result of acidification, the sample is ready to titrate.

18. Use a clean, graduated cylinder to transfer 200 mL of the solution to a 300-mL BOD bottle or Erlenmeyer flask.
19. Place the flask on a magnetic stirrer, if this equipment is available. Otherwise, use a pipet and bulb, swirling the sample by hand.
20. Stir the sample at a moderate rate without aerating the sample. Titrate with 0.025N PAO until the solution is pale straw-yellow in color.
21. Add 1 to 2 mL of stable starch reagent and note the blue color, which indicates the presence of iodine. A few drops should give the blue indicator color (not gray). If more than 1 or 2 mL are needed to produce the color, the sample titration results should be rejected and the starch solution replaced.
22. Continue the titration just until the blue color disappears. Do titration against a white background. This step requires either continuous stirring or vigorous swirling to ensure that the titration endpoint is accurate. Disregard the reappearance of the blue color after a few minutes.

The total volume (in milliliters) of PAO used in the titration is equal to the DO concentration, expressed in milligrams per liter. The DO concentration from the titration should be recorded to the nearest 0.1 mg/L. For a 200-mL sample, the volume of titrant added is directly proportional to the DO concentration in milligrams per liter. To compute DO for a sample greater or less than 200 mL, use the following formula:

$$\text{DO (mg/L)} = \frac{200}{\text{sample volume} \times \text{titrant added (in mL)}} \times \text{volume of PAO used (in mL)}$$

Corrections to Dissolved Oxygen Measurements Made With Dissolved Oxygen Meters

Some DO meters report measurements that are not compensated for salinity. Field DO measured with meters that are not salinity compensated and that are measured in waters with specific conductance exceeding 1,800 µS/cm, must be corrected. This correction is made by multiplying the field DO concentrations by a correction factor, which is computed from the following formula:

$$F = 1 - \frac{[0.003439 + 0.361] C}{(22.1 + T)^2 \times 1,000},$$

where

F = adjustment factor;

T = water temperature in degrees Celsius; and

C = specific conductance in microsiemens per centimeter,

Corrected DO = field DO x F.

The sample collector should record the corrected DO concentration.